

## PATENT ABSTRACTS OF JAPAN

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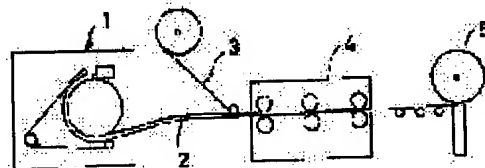
TAKAHASHI KATSUHIRO

## (54) ELECTRODE PLATE FOR LEAD-ACID BATTERY AND LEAD-ACID BATTERY USING THE ELECTRODE PLATE

(57)Abstract:

PURPOSE: To improve the adhesive property of a grid and an active material, and to increase the service life property, by making a part or the whole body of the crystal formation inside a grid alloy to a recrystallization formation, after filling a paste to be an active material to a grid body prior to the recrystallization.

CONSTITUTION: A slab made of a Pb-Ca-Sn alloy casted by a slab casting machine 1, and a Pb-Sb-Sn alloy foil 3 are delivered to a rolling machine 4 in the condition superposing both members, so as to be rolled, and a lead alloy sheet 5 on which the Pb-Sb-Sn alloy is coated is obtained. And after the sheet 5 is produced, it is expanding processed as in the condition the crystal formation is the rolled formation, a paste is filled, a heat treatment at 60°C or higher is applied, and a part of the grid formation is recrystallized. As a result, when the grid in the rolled formation condition is transferred to the recrystallization formation partially by the heat in the aging drying of the grid, the grid is contracted to a specific height. In such a way, the active material and the grid are adhered strongly, and the service life property is improved.



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CLAIMS

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[Claim]

[Claim 1] The plate for lead accumulators which the cold rolling of the slab of a lead-calcium-tin system alloy is carried out at the temperature of 120 degrees C or less, and it considers as the lead-alloy sheet which has a precise rolling organization in the interior of an alloy, an expanded manipulation etc. is machined and this is made into the grid field in front of a recrystallization, and made the recrystallized structure a part or all of the crystalline structure inside a grid alloy after filling up with the paste used as an active material.

[Claim 2] The plate for lead accumulators of the claim 1 publication characterized by having heat-treated at the temperature of 60 degrees C or more, and making a part or all of the crystalline structure inside a grid alloy into a recrystallized structure after filling up with the paste used as an active material.

[Claim 3] The claim 1 characterized by making concentration of calcium into 0.05 - 0.08% of a domain for the concentration of the tin to add 0.5 to 2.0%, or the plate for lead accumulators given in two.

[Claim 4] formation -- the claim 1 characterized by using a paste which increases 1% or more compared with the volume before a next volume degassing, or the plate for lead accumulators given in either of 3

[Claim 5] The claim 1 characterized by using as an anode plate, or the plate for lead accumulators given in either of 4.

[Claim 6] The lead accumulator characterized by using the aforementioned claim 1 or the plate for lead accumulators given in either of 5.

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## DETAILED DESCRIPTION

[Detailed description]

[0001]

[Field of the Invention] this invention relates to an improvement of the life property of enhancement of a lead accumulator especially the maintenance-free type which used the lead-calcium-tin system alloy for the anode plate grid, and the so-called calcium system lead accumulator, especially an improvement of an elevated-temperature life property.

[0002]

[Prior art] The lead accumulator which used the lead-calcium-tin system alloy for the positive cathode grid field has the characteristic features, like that there is little self-discharge and the store property are excellent, and is called maintenance-free cell.

[0003] Instead, the technique of carrying out the expanded manipulation of the tin-alloy sheet which rolled out such an alloy system in the cell used for a grid, and using as the grid field has spread widely for the casting till then.

[0004] However, generally it is known that the lead accumulator which used such a lead-calcium-tin system alloy for the anode plate will tend to produce the cell performance degradation which originates in a fall of the adhesion of a grid and an active material compared with the cell which used the lead-antimony system alloy for the anode plate.

[0005] When cubical expansion is carried out in the process in which an anode plate grid carries out the oxidization cauterization and the whole grid deforms while in use as one of these causes for the reason, producing a void is raised between an active material and a grid.

[0006] Moreover, although another cause will start melting into an active material gradually and will make adhesion of an active material and a grid good while it uses it if antimony is contained in the grid, that antimony is not contained also influences a lead-calcium-tin system alloy. The one technique of solving the former cause is preparing the alloy with high tensile strength so that the force which improves more, and oxidizes and carries out cubical expansion of the oxidation resistance of a grid alloy can be overcome. About this, it has turned out that it is an effective means to make high tin concentration in a lead-calcium-tin system alloy in less than 2.0% of the domain.

[0007] Technique, such as sticking a lead-antimony system alloy on the front face of a lead-alloy sheet as a means to solve the latter cause, is devised.

[0008]

[Object of the Invention] Thus, by the cell which uses a lead-calcium-tin system alloy for the anode plate grid field, efforts of an improvement have been concentrated on how [ physically or / chemical ] the adhesion of a grid and an active material is raised until now. this invention raises the adhesion of a grid and an active material physically by the principle different from the former, and it aims at aiming at an improvement of a life property, especially the life property in an elevated temperature.

[0009]

[The means for solving a technical problem] The electrode for lead accumulators of this invention carries out the cold rolling of the slab of a lead-calcium-tin system alloy at the temperature of 120 degrees C or less that the aforementioned purpose should be attained. Consider as the lead-alloy sheet which has a precise rolling organization in the interior of an alloy, and in front of a recrystallization, machine an expanded manipulation etc. and this is made into the grid field. After filling up with the paste used as an active material, a part or all of the crystalline structure inside a grid alloy is made into a recrystallized structure, and the lead accumulator of this invention uses the aforementioned electrode for lead accumulators as an electrode.

[0010] After filling up the aforementioned recrystallization with the paste used as an active material, it is desirable to heat-treat at the temperature of 60 degrees C or more, and to make a part or all of the crystalline structure inside a grid

alloy into a recrystallized structure.

[0011] Moreover, it is desirable to make concentration of calcium into 0.05 - 0.08% of a domain for the concentration of the tin to add 0.5 to 2.0%.

[0012] moreover -- the aforementioned paste \*\*\*\*\* -- formation -- it is desirable to use a paste which increases 1% or more compared with the volume before a next volume degassing

[0013] Moreover, as for the aforementioned electrode for lead accumulators, using as an anode plate is desirable. Moreover, a life can be more raised by giving a lead-antimony-tin system alloy to a part of front face of the aforementioned lead-alloy sheet, or front face.

[0014]

[Operation] The tin-calcium-tin system alloy by which the cold rolling was carried out has a precise rolling organization immediately after rolling. This organization changes to a stable recrystallization nature organization with time progress. This change happens early so that temperature is high. With formation of this recrystallized structure, to the grain boundary of the crystalline structure, the compound of lead, calcium, or tin and calcium generates, and the mechanical intensity of a lead-alloy sheet improves. When the rolling sheet of this lead-calcium-tin system alloy changed to a recrystallized structure this time, it was presumed from the result that whose a grid causes deflation slightly it is an experiment. Therefore, after having used this lead-alloy sheet as the grid field by expanded manipulation etc. and filling up with a paste before recrystallization, by making this grid field recrystallize showed the grid field itself causing deflation slightly and being mechanically stuck to a grid and an active material strongly.

[0015] moreover, an active material -- formation -- if it chooses so that the intumescence at the time may become large, the mechanical adhesion force of a grid and an active material can be raised more formation -- in order to enlarge the intumescence at the time, it is effective to add a minium etc. for example, during the paste

[0016] The concentration of tin of the alloy composition which demonstrates such an effect most and actually has an effect in the enhancement in a life was, while the concentration of 0.5 - 2.0% and calcium was 0.05 - 0.08%. Since enhancement in the adhesion of a chemical grid and an active material can also be simultaneously aimed at if processing same about what furthermore gave the lead-antimony-tin system alloy to a part of front face of a lead-alloy sheet or front face is performed, there is an effect of much more enhancement in a life.

[0017]

[Example] Below, an example explains this invention.

(Experiment 1) After having melted the tin alloy -0.07% calcium-1.0% of lead and making it into slab with 10mm [ in thickness ], and a width of face of 80mm, it rolled out and considered as the rolling sheet with a thickness of 1.0mm.

[0018] Moreover, the rolling sheet which coated the front face with the tin alloy by the same composition -5% antimony-5% of lead was also produced simultaneously. The schematic diagram of the plate for lead accumulators obtained from the sheet which produced the production technique of the sheet at this time again to drawing 1 is shown in drawing 2.

[0019] As shown in drawing 1, where the slab made from a Pb-calcium-Sn alloy 2 and the Pb-Sb-Sn alloy foil 3 which were cast in the slab casting machine 1 are piled up, it sent in and rolled out to the rolling mill 4, and the lead-alloy sheet 5 which coated the Pb-Sb-Sn alloy was obtained.

[0020] By the enlarged section of the grid bone which 11 show a plate among drawing 2, and 12 shows an expanded metal grating bone, and is shown by A in drawing, 13 shows a Pb-Sb-Sn alloy coating layer and 14 shows a Pb-calcium-Sn alloy grid bone.

[0021] The part was left in 60 degrees C in the state of the sheet about these sheets for 48 hours. At this time, some of rolling organization changed to the recrystallized structure. The expanded manipulation was carried out in this status, and it was filled up with the paste and considered as the plate. Moreover, about other parts, while the crystalline structure after sheet production had been in the status of a rolling organization, the expanded manipulation was performed, it was filled up with the paste, heat treatment of 48 hours was performed at 60 degrees C after that, and the organization of a part of grid was made to recrystallize. A cell is produced using such a plate and it is JIS at 75 degrees C. D Light load life test of 5301 was performed. The result is shown in Table 1. What this was mulled by water and the dilute sulfuric acid according to constant law, and was made into the shape of a paste was used using what contains the fine particles of the plumbic-acid ghost which contains the minium other than the powder which becomes a lead powder from a usual plumbic-acid ghost and usual metal lead at this time 80% 20%.

[0022]

[Table 1]

電池 N o	極板の製造方法	コーティング	寿命回数
A	圧延組織のまま で格子に加工	なし	4 2 0 0
B	圧延組織のまま で格子に加工	あり	7 0 0 0
C	再結晶組織後を 格子に加工	なし	1 8 0 0
D	再結晶組織後を 格子に加工	あり	2 4 0 0

[0023] The expanded manipulation of the lead sheet with the status of a rolling organization is carried out like [ as a result of Table 1 ]. The way of the cell (A, B) using the plate which the grid recrystallized when digestion xeransis was carried out after that heat-treats a lead sheet. compared with the cell (C, D) which carried out the expanded manipulation of what was partially made into the recrystallized structure, was filled up with the paste and made into the plate, a life is markedly alike, it is long and a \*\*\*\*\* understands [ the way at the time of coating a sheet front face with a lead-antimony system alloy also in it ] a life At this time, when the height of a plate was measured, by C and D, it had contracted only 0.5mm to having contracted the plate of A and B 1.2mm from xeransis before after digestion xeransis (the height of an early plate is 100mm). moreover, formation -- a next height -- A and B -- formation -- a front -- 1.0mm, i.e., it was extended about 1% and had contracted 0.2mm from the first stage, -- receiving -- C and D -- formation -- it is extended 1.0mm from a front and having been extended 0.5mm was observed from the first stage

[0024] When shifting to a recrystallized structure partially from the above thing with heat in case the grid of the status of a rolling organization is digestion xeransis, it turns out that a grid carries out configuration change which is contracted in the height orientation. Consequently, the force in which it is strongly stuck to an active material and a works, and it is considered by this for a life to improve. moreover, a plate -- formation -- although cubical expansion is caused behind, it is thought that the adhesion of a grid and an active material improves more conjointly with this

[0025] In addition, the organization of the sheet in cells A and B, i.e., a rolling organization, and the organization of the sheet in cells C and D, i.e., the status are a recrystallized structure partially, are shown in the \*\* type view of drawing 3. Moreover, although it doubles and the metal texture of the grid of each cell is shown simultaneously, it turns out that both are recrystallized structures partially.

(Experiment 2) this formation -- in order to investigate the effect by intumescence of the active material at the time -- prescription of a paste -- changing -- formation -- the comparison by the active material from which a volume change [ before and after ] differs was performed Sake [ comparison-], the life test result of cell F which used the same paste on condition that cell D is shown with cell E to which the life made the paste only from the lead powder which consists of usual plumbic-acid ghost powder and a usual metal lead powder on condition that longest cell B in Table 2. E and F were short to the corresponding cells B and D, and the result of life test had the large fall of the life of E especially to B. although deflation of the plate of E and F was the same as that of B and D after digestion xeransis when height change of a plate was measured -- formation -- next elongation -- formation -- it did not pass from a front to 0.5mm, i.e., about 0.5% this -- formation -- when the cubical expansion of a next active material is 1% or more showed that it was more effective

[0026]

[Table 2]

電池 N o	極板の製造方法	コーティング	寿命回数	備考
E	圧延組織のまま で格子に加工	あり	4 0 0 0	B, Dとペ ーストが異 なる
F	再結晶組織後を 格子に加工	あり	2 0 0 0	

[0027] In order to investigate still in detail, change of a life was investigated by composition of a lead-calcium-tin

system alloy. The result is shown in drawing 4. The addition of tin and calcium shows that a life changes remarkably from this drawing. This is based on the corrosion resistance in each alloy composition, and a mechanical strength. This drawing shows that 0.05 - 0.08% of a domain is suitable as a concentration domain of calcium 0.5 to 2.0% as a concentration domain of tin.

[0028] Moreover, by this invention, like, in the state of the lead sheet, although the thing which was described above and for which a recrystallized structure is formed in the state of a grid in a rolling organization was important, in order not to form a recrystallized structure in the state of a lead sheet, it was confirmed by another experiment that it is also effective to perform strip processing at the temperature of 120 degrees C or less.

[0029]

[Effect of the invention] According to this invention, the life under the elevated temperature of the lead accumulator using the grid field which machined the expanded manipulation etc. on the rolling sheet of a lead-calcium-tin system alloy, and was acquired on it is notably improvable as mentioned above.

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**TECHNICAL FIELD**

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**PRIOR ART**

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[Prior art] The lead accumulator which used the lead-calcium-tin system alloy for the positive cathode grid field has the characteristic features, like that there is little self-discharge and the store property are excellent, and is called maintenance-free cell.

[0003] Instead, the technique of carrying out the expanded manipulation of the tin-alloy sheet which rolled out such an alloy system in the cell used for a grid, and using as the grid field has spread widely for the casting till then.

[0004] However, generally it is known that the lead accumulator which used such a lead-calcium-tin system alloy for the anode plate will tend to produce the cell performance degradation which originates in a fall of the adhesion of a grid and an active material compared with the cell which used the lead-antimony system alloy for the anode plate.

[0005] When cubical expansion is carried out in the process in which an anode plate grid carries out the oxidation cauterization and the whole grid deforms while in use as one of these causes for the reason, producing a void is raised between an active material and a grid.

[0006] Moreover, although another cause will start melting into an active material gradually and will make adhesion of an active material and a grid good while it uses it if antimony is contained in the grid, that antimony is not contained also influences a lead-calcium-tin system alloy. The one technique of solving the former cause is preparing the alloy with high tensile strength so that the force which improves more, and oxidizes and carries out cubical expansion of the oxidation resistance of a grid alloy can be overcome. About this, it has turned out that it is an effective means to make high tin concentration in a lead-calcium-tin system alloy in less than 2.0% of the domain.

[0007] Technique, such as sticking a lead-antimony system alloy on the front face of a lead-alloy sheet as a means to solve the latter cause, is devised.

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**EFFECT OF THE INVENTION**

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[Effect of the invention] According to this invention, the life under the elevated temperature of the lead accumulator using the grid field which machined the expanded manipulation etc. on the rolling sheet of a lead-calcium-tin system alloy, and was acquired on it is notably improvable as mentioned above.

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**TECHNICAL PROBLEM**

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[Object of the Invention] Thus, by the cell which uses a lead-calcium-tin system alloy for the anode plate grid field, efforts of an improvement have been concentrated on how [ physically or / chemical ] the adhesion of a grid and an active material is raised until now. this invention raises the adhesion of a grid and an active material physically by the principle different from the former, and it aims at aiming at an improvement of a life property, especially the life property in an elevated temperature.

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**MEANS**

[The means for solving a technical problem] The electrode for lead accumulators of this invention carries out the cold rolling of the slab of a lead-calcium-tin system alloy at the temperature of 120 degrees C or less that the aforementioned purpose should be attained. Consider as the lead-alloy sheet which has a precise rolling organization in the interior of an alloy, and in front of a recrystallization, machine an expanded manipulation etc. and this is made into the grid field. After filling up with the paste used as an active material, a part or all of the crystalline structure inside a grid alloy is made into a recrystallized structure, and the lead accumulator of this invention uses the aforementioned electrode for lead accumulators as an electrode.

[0010] After filling up the aforementioned recrystallization with the paste used as an active material, it is desirable to heat-treat at the temperature of 60 degrees C or more, and to make a part or all of the crystalline structure inside a grid alloy into a recrystallized structure.

[0011] Moreover, it is desirable to make concentration of calcium into 0.05 - 0.08% of a domain for the concentration of the tin to add 0.5 to 2.0%.

[0012] moreover -- the aforementioned paste \*\*\*\*\* -- formation -- it is desirable to use a paste which increases 1% or more compared with the volume before a next volume degassing

[0013] Moreover, as for the aforementioned electrode for lead accumulators, using as an anode plate is desirable. Moreover, a life can be more raised by giving a lead-antimony-tin system alloy to a part of front face of the aforementioned lead-alloy sheet, or front face.

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**OPERATION**

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[Operation] The tin-calcium-tin system alloy by which the cold rolling was carried out has a precise rolling organization immediately after rolling. This organization changes to a stable recrystallization nature organization with time progress. This change happens early so that temperature is high. With formation of this recrystallized structure, to the grain boundary of the crystalline structure, the compound of lead, calcium, or tin and calcium generates, and the mechanical intensity of a lead-alloy sheet improves. When the rolling sheet of this lead-calcium-tin system alloy changed to a recrystallized structure this time, it was presumed from the result that whose a grid causes deflation slightly it is an experiment. Therefore, after having used this lead-alloy sheet as the grid field by expanded manipulation etc. and filling up with a paste before recrystallization, by making this grid field recrystallize showed the grid field itself causing deflation slightly and being mechanically stuck to a grid and an active material strongly.

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[0016] The concentration of tin of the alloy composition which demonstrates such an effect most and actually has an effect in the enhancement in a life was, while the concentration of 0.5 - 2.0% and calcium was 0.05 - 0.08%. Since enhancement in the adhesion of a chemical grid and an active material can also be simultaneously aimed at if processing same about what furthermore gave the lead-antimony-tin system alloy to a part of front face of a lead-alloy sheet or front face is performed, there is an effect of much more enhancement in a life.

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## EXAMPLE

[Example] Below, an example explains this invention.

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[0018] Moreover, the rolling sheet which coated the front face with the tin alloy by the same composition -5% antimony-5% of lead was also produced simultaneously. The schematic diagram of the plate for lead accumulators obtained from the sheet which produced the production technique of the sheet at this time again to drawing 1 is shown in drawing 2.

[0019] As shown in drawing 1, where the slab made from a Pb-calcium-Sn alloy 2 and the Pb-Sb-Sn alloy foil 3 which were cast in the slab casting machine 1 are piled up, it sent in and rolled out to the rolling mill 4, and the lead-alloy sheet 5 which coated the Pb-Sb-Sn alloy was obtained.

[0020] By the enlarged section of the grid bone which 11 show a plate among drawing 2, and 12 shows an expanded metal grating bone, and is shown by A in drawing, 13 shows a Pb-Sb-Sn alloy coating layer and 14 shows a Pb-calcium-Sn alloy grid bone.

[0021] The part was left in 60 degrees C in the state of the sheet about these sheets for 48 hours. At this time, some of rolling organization changed to the recrystallized structure. The expanded manipulation was carried out in this status, and it was filled up with the paste and considered as the plate. Moreover, about other parts, while the crystalline structure after sheet production had been in the status of a rolling organization, the expanded manipulation was performed, it was filled up with the paste, heat treatment of 48 hours was performed at 60 degrees C after that, and the organization of a part of grid was made to recrystallize. A cell is produced using such a plate and it is JIS at 75 degrees C. D Light load life test of 5301 was performed. The result is shown in Table 1. What this was mulled by water and the dilute sulfuric acid according to constant law, and was made into the shape of a paste was used using what contains the fine particles of the plumbic-acid ghost which contains the minium other than the powder which becomes a lead powder from a usual plumbic-acid ghost and usual metal lead at this time 80% 20%.

[0022]

[Table 1]

電池 N O	極板の製造方法	コーティング	寿命回数
A	圧延組織のまま で格子に加工	なし	4 2 0 0
B	圧延組織のまま で格子に加工	あり	7 0 0 0
C	再結晶組織後を 格子に加工	なし	1 8 0 0
D	再結晶組織後を 格子に加工	あり	2 4 0 0

[0023] The expanded manipulation of the lead sheet with the status of a rolling organization is carried out like [ as a result of Table 1 ]. The way of the cell (A, B) using the plate which the grid recrystallized when digestion xeransis was carried out after that heat-treats a lead sheet. compared with the cell (C, D) which carried out the expanded manipulation of what was partially made into the recrystallized structure, was filled up with the paste and made into the

plate, a life is markedly alike, it is long and a \*\*\*\*\* understands [ the way at the time of coating a sheet front face with a lead-antimony system alloy also in it ] a life At this time, when the height of a plate was measured, by C and D, it had contracted only 0.5mm to having contracted the plate of A and B 1.2mm from xeransis before after digestion xeransis (the height of an early plate is 100mm). moreover, formation -- a next height -- A and B -- formation -- a front -- 1.0mm, i.e., it was extended about 1% and had contracted 0.2mm from the first stage, -- receiving -- C and D -- formation -- it is extended 1.0mm from a front and having been extended 0.5mm was observed from the first stage [0024] When shifting to a recrystallized structure partially from the above thing with heat in case the grid of the status of a rolling organization is digestion xeransis, it turns out that a grid carries out configuration change which is contracted in the height orientation. Consequently, the force in which it is strongly stuck to an active material and a works, and it is considered by this for a life to improve. moreover, a plate -- formation -- although cubical expansion is caused behind, it is thought that the adhesion of a grid and an active material improves more conjointly with this [0025] In addition, the organization of the sheet in cells A and B, i.e., a rolling organization, and the organization of the sheet in cells C and D, i.e., the status are a recrystallized structure partially, are shown in the \*\* type view of drawing 3 . Moreover, although it doubles and the metal texture of the grid of each cell is shown simultaneously, it turns out that both are recrystallized structures partially.

(Experiment 2) this formation -- in order to investigate the effect by intumescence of the active material at the time -- prescription of a paste -- changing -- formation -- the comparison by the active material from which a volume change [ before and after ] differs was performed Sake [ comparison-], the life test result of cell F which used the same paste on condition that cell D is shown with cell E to which the life made the paste only from the lead powder which consists of usual plumbic-acid ghost powder and a usual metal lead powder on condition that longest cell B in Table 2. E and F were short to the corresponding cells B and D, and the result of life test had the large fall of the life of E especially to B. although deflation of the plate of E and F was the same as that of B and D after digestion xeransis when height change of a plate was measured -- formation -- next elongation -- formation -- it did not pass from a front to 0.5mm, i.e., about 0.5% this -- formation -- when the cubical expansion of a next active material is 1% or more showed that it was more effective

[0026]

[Table 2]

電池 N O	極板の製造方法	コーティング	寿命回数	備考
E	圧延組織のまま で格子に加工	あり	4 0 0 0	B, D とベ ーストが異 なる
F	再結晶組織後を 格子に加工	あり	2 0 0 0	

[0027] In order to investigate still in detail, change of a life was investigated by composition of a lead-calcium-tin system alloy. The result is shown in drawing 4 . The addition of tin and calcium shows that a life changes remarkably from this drawing. This is based on the corrosion resistance in each alloy composition, and a mechanical strength. This drawing shows that 0.05 - 0.08% of a domain is suitable as a concentration domain of calcium 0.5 to 2.0% as a concentration domain of tin.

[0028] Moreover, by this invention, like, in the state of the lead sheet, although the thing which was described above and for which a recrystallized structure is formed in the state of a grid in a rolling organization was important, in order not to form a recrystallized structure in the state of a lead sheet, it was confirmed by another experiment that it is also effective to perform strip processing at the temperature of 120 degrees C or less.

[Translation done.]



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DESCRIPTION OF DRAWINGS

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[An easy explanation of a drawing]

[ Drawing 1 ] The \*\* type view of the process which rolls out a Pb-calcium-Sn alloy and produces a lead-alloy sheet while coating a front face with a Pb-Sb-Sn alloy

[ Drawing 2 ] The schematic diagram of the plate for lead accumulators obtained from the aforementioned lead-alloy sheet

[ Drawing 3 ] The \*\* type view showing the crystallized state of the lead-alloy sheet used for each cell, and a grid bone

[ Drawing 4 ] The property view showing the relation between calcium and Sn concentration, and the number of times of life test

[An explanation of a sign]

1 Slab Casting Machine

2 Slab made from Pb-Calcium-Sn Alloy

3 Pb-Sb-Sn Alloy Foil

4 Rolling Mill

5 Lead-Alloy Sheet

11 Plate

12 Expanded Metal Grating Bone

13 Pb-Sb-Sn Alloy Coating Layer

14 Pb-Calcium-Sn Alloy Grid Bone

A Grid bone cross section

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[Translation done.]

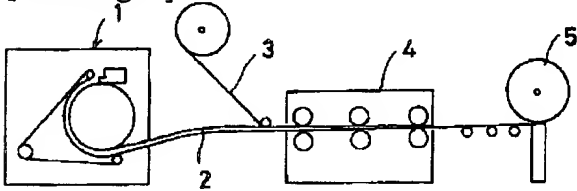
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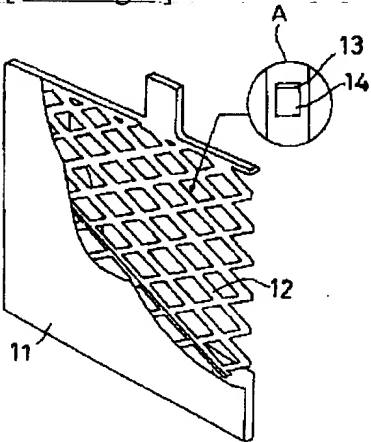
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## DRAWINGS

[ Drawing 1 ]

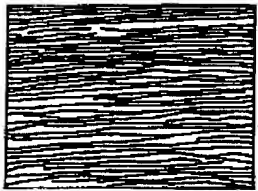


[ Drawing 2 ]



[ Drawing 3 ]

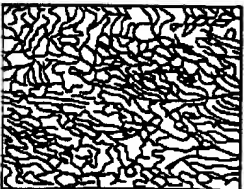
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(B)



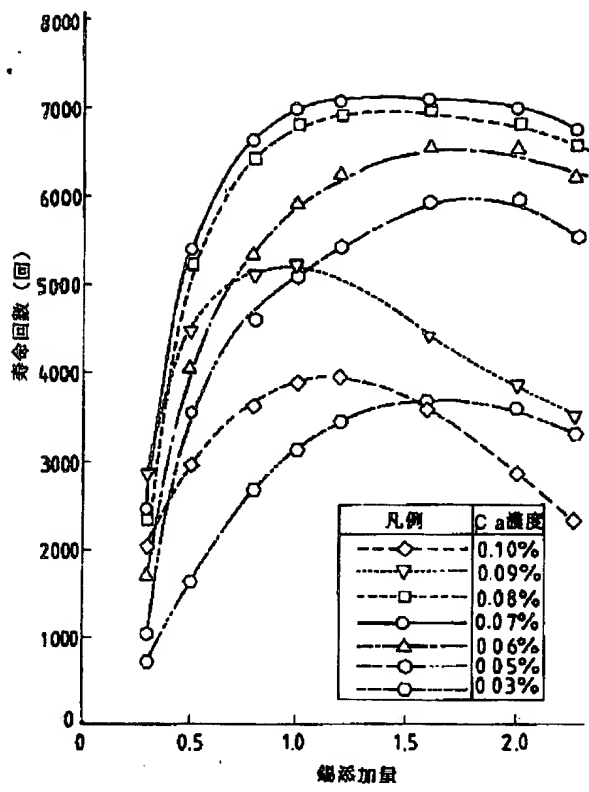
(C)



(D)



[ Drawing 4 ]



[Translation done.]

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## CORRECTION or AMENDMENT

[Official report class] Printing of the amendment by the convention of 2 of Article 17 of a patent law  
 [Section partition] The 7th section 1st partition  
 [Issue date] December 24, Heisei 11 (1999)

[A open number] Publication number 6-267544  
 [A open day] September 22, Heisei 6 (1994)  
 [\*\*\*\* format] Open patent official report 6-2676  
 [Application number] Japanese Patent Application No. 5-51923  
 [The 6th edition of International Patent Classification]

H01M 4/74  
 4/14  
 4/73

## [FI]

H01M 4/74 B  
 4/14 Q  
 4/73 A

## [Procedure revision]

[Presentation day] March 15, Heisei 11

## [Procedure amendment 1]

[The document name for an amendment] Specification

[The subject name for an amendment] 0003

[The amendment technique] Change

[Content of an amendment]

[0003] Instead, the technique of carrying out the expanded manipulation of the lead-alloy sheet which rolled out such an alloy system in the cell used for a grid, and using as the grid field has spread widely for the casting till then.

## [Procedure amendment 2]

[The document name for an amendment] Specification

[The subject name for an amendment] 0009

[The amendment technique] Change

[Content of an amendment]

[0009]

[The means for solving a technical problem] The cold rolling of the slab of a lead-calcium-tin system alloy is carried out at the temperature of 120 degrees C or less that the plate for lead accumulators of this invention should attain the aforementioned purpose. Consider as the lead-alloy sheet which has a precise rolling organization in the interior of an alloy, and in front of a recrystallization, machine an expanded manipulation etc. and this is made into the grid field. After filling up with the paste used as an active material, a part or all of the crystalline structure inside a grid alloy is made into a recrystallized structure, and the lead accumulator of this invention uses the aforementioned plate for lead accumulators as an anode plate.

[Procedure amendment 3]

[The document name for an amendment] Specification

[The subject name for an amendment] 0013

[The amendment technique] Change

[Content of an amendment]

[0013] Moreover, as for the aforementioned plate for lead accumulators, using as an anode plate is desirable. Moreover, a life can be more raised by giving a lead-antimony-tin system alloy to a part of front face of the aforementioned lead-alloy sheet, or front face.

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[Translation done.]